

STUDIES ON THE INFLUENCE OF COMPOSITION AND
TEMPERATURE ON THE ELECTRICAL CONDUCTIVITY
OF SOME ALKALINE EARTH TITANATES

BY

ISRAEL ARNOLD LESK

B.Sc., University of Alberta, 1948

M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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UNIVERSITY OF ILLINOIS, 1951

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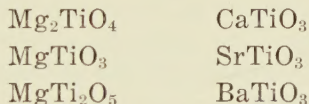
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STUDIES ON THE INFLUENCE OF COMPOSITION AND TEMPERATURE ON THE ELECTRICAL CONDUCTIVITY OF SOME ALKALINE EARTH TITANATES

The object of this investigation was to contribute to the better understanding of semi-conducting raw materials by an exploratory study of the resistivities of the titanates of magnesium, calcium, strontium and barium. These compounds, both with stoichiometric composition and in various stages of reduction, were to be investigated over the temperature range from 30°C. to within 100°C. of their melting points. Sintered bodies rather than single crystals were to be used.

A study of the literature revealed the identification and method of preparation of the following stable titanates of the four alkaline-earth elements mentioned above:



Crystal structures of these compounds were discussed.

Each of these six alkaline-earth titanates was prepared by the method of reaction in the solid state. Components were mixed together in a ball mill for a total of 20 hours, and heated at 1300°C. for a total of 45 hours, in order to insure thorough mixing and compound formation. CaTiO_3 was prepared by mixing CaCO_3 and TiO_2 in a molecular ratio of 1:1. SrTiO_3 and BaTiO_3 were made similarly. Each of the magnesium titanates was prepared from a mixture of MgO and TiO_2 . The MgO from different parts of stock contained different amounts of volatile impurities, and the MgO itself was quite volatile, so that a different method had to be chosen for the formation of the magnesium titanates. Accordingly, a little MgO was added in excess of that specified by the molar ratio of $\text{MgO}:\text{TiO}_2$ for each of the magnesium compounds, and a

chemical method used to remove unwanted MgO and magnesium titanates after formation.

The impurity content of each of the alkaline-earth titanates produced was checked by means of X-ray powder diffraction analysis. The sensitivity of this method was of the order of 1 to 3%.

The powdered titanates were prepared into rod form by mixing with a starch binder, packing inside a glass tube, and pushing the core so formed out of the glass tube.

For high temperature measurements, a furnace with directly heated platinum coil was made. The atmosphere inside the furnace could be controlled to be one of hydrogen, helium, or oxygen.

All titanate rods were sintered in an oxygen atmosphere to a temperature of 1450°C. and cut to a length of 15.0 mm. The densities of the compounds in rod form were all within 8% of the X-ray densities of the compounds. Platinum end caps were applied to the rods by coating the ends with platinum paste and driving off the solvent by heating in a non-reducing torch flame.

The resistance vs. temperature characteristics of the unreduced compounds were measured in an oxygen atmosphere, up to 1400°C.

Reduction of the other rods was done at high temperatures in a hydrogen atmosphere. Attempts made to measure the resistance vs. temperature characteristics of the reduced rods in helium failed because a sufficiently non-aggressive atmosphere could not be obtained. The resistances were never found to follow the same heating and cooling curves, indicating oxidation or reduction during the measurements. The use of an evacuated furnace also failed to give reproducible results.

The following facts led to the development of a method for measuring resistance vs. temperature characteristics of the

reduced titanate rods. (1) In 10 seconds, the resistance of a reduced rod covered more than 90% of its resistance change after a sudden temperature drop from 30°C. to -70°C. (2) In the range of reduction temperatures planned, 10 seconds was much less than the time taken for the furnace to cool 100°C. after the heater power was suddenly cut off. (3) When the furnace atmosphere was changed from helium to hydrogen at a high temperature, the resistance of a rod dropped, quickly at first, but very slowly after about 10 minutes, indicating a levelling off of the amount of reduction after a sufficiently long time. The amount of reduction increased as the reducing temperature was increased. Considering the above three factors, the method of resistance vs. temperature measurement used was to (1) heat the rods in helium to the desired temperature, (2) change the atmosphere to one of hydrogen and allow reduction to take place for 15 minutes, (3) suddenly remove the power supplying the furnace heater, and (4) take resistance and temperature readings in a hydrogen atmosphere as the furnace cooled.

Movable probe measurements at room temperature, and fixed probe measurements over the range of temperatures from -70°C. to 70°C. revealed good linearity of potential distribution along the rods, and small variation of the contact resistance between rod and end cap with temperature. Accordingly, the resistivity of an alkaline-earth titanate was found by multiplying the rod resistance by the ratio of its cross-sectional area to length.

A family of curves, plotted as logarithm of resistivity vs. reciprocal absolute temperature, was obtained for each of the alkaline-earth titanates made. The range of resistivity values measured was between 10^{-1} and 10^8 ohm.-cm., and temperatures from 30°C. to as high as 1400°C. were used. The curve for the unreduced sample of each family had a very steep slope. Curves for the reduced samples, at lower temperatures, were straight lines with slopes successively smaller the larger was the amount of reduction. At temperatures close to those at which reduction was done, the curves for CaTiO_3 , SrTiO_3 ,

and BaTiO_3 joined one another, but at temperatures reached did not join the line representing the unreduced sample. The curves in the magnesium titanate families exhibited no joining at all in the temperature range used.

Room-temperature resistivity, and rate of change of this resistivity with temperature, varied markedly for the different compounds with similar degrees of reduction.

In the neighborhood of 115°C ., curves for reduced BaTiO_3 exhibited changes of slope of more than 50% in some cases. This may be attributed to the BaTiO_3 crystal structure change that occurs at 120°C .

The amounts of reduction of the more heavily reduced samples of each of the titanates were determined by reoxidizing back to stoichiometry, and determining the percent gain in weight. Reductions up to about 2% by weight were given the most reduced magnesium titanates, while the most reduced samples of CaTiO_3 , SrTiO_3 and BaTiO_3 had lost less than about 0.2% of their masses. Hence, reducing a titanate rod a slight amount was found to change its room-temperature resistivity by a factor of as large as 10^9 .

The number of impurity donors in the alkaline-earth titanates resulting from reduction was calculated for each case where the percent reduction of the sample could be determined by weighing.

The largest number of reductions that could be determined by weighing was in the case of Mg_2TiO_4 . Using experimental data, variations of Fermi and donor levels with percent reduction and resistivity at a given temperature were calculated for this compound. The slopes of these curves were found to diminish a small amount for the larger percent reductions.

Factors were considered for the practical application of the magnesium titanates as thermistor materials.

VITA

Israel Arnold Lesk was born on January 26, 1927, in Regina, Saskatchewan, Canada. He graduated from Alexandra High School in Medicine Hat, Alberta, Canada in 1944 and was awarded a Matriculation Scholarship by the University of Alberta. Among the awards he won there were the Board of Governors' prize for first year Applied Science, the Gas Company Scholarship for the first two years of Engineering, and the Engineering Institute of Canada prize for third year Applied Science. He received his B.Sc. degree with high distinction in Engineering Physics from the University of Alberta in 1948, at the same time being awarded the Henry Birks and Sons gold medal for Applied Science. He also won the Galvin Fellowship in Electrical Engineering at the University of Illinois, where he began his graduate work in 1948. In 1949 he received his M.S. degree from the University of Illinois. At that institution he held a half-time teaching assistantship from 1949 to 1951, and a research assistantship during the summer of 1951. He is a member of Sigma Xi, Phi Kappa Phi, Eta Kappa Nu, and Pi Mu Epsilon.



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